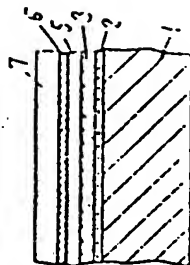


91-107476/15 A89 E24 G06 W04 (T03) MATU 19.07.89  
WATSUSHITA ELEC IND KK \*JO 3051-182-A  
19.07.89-JP-186417 (05.03.91) B41m-05/26 G11b-07/24  
Humidity resistant optical information recording medium - has  
recording layer confg. optically stabilised organic pigment on  
transparent substrate  
C91-046443

A(12-13C) E(21, 25-B) G(6-C6, 6-D7, 6-F4, 6-F5)

A 0897

with good humidity resistance, which is stable to the environment  
light or repeatedly given regenerating light is obtd. (6pp  
Dwg.No.7/10)



A recording layer confg. an optically stabilised organic pigment (which is made of an anion of an electron accepting azo type metal complex salt and a cyanine pigment cation having its absorption in a wave length region of the recording light) is provided on a transparent substrate.

The optical recording medium is made of (1) at least a recording layer, a reflection layer (made of a metal) and a protection layer laminated on a transparent substrate in this order; (2) at least a recording layer, an intermediate layer made of a transparent resin, a reflection layer (made of a metal) and a protection layer laminated on a transparent substrate in this order; (3) at least a recording layer, an intermediate layer made of a resin, and a protection layer laminated on a transparent substrate in this order; or (4) at least a recording layer, and a protection layer laminated on a transparent substrate in this order. The recording layer pref. contains a resin and another pigment having different absorption max from that of the optically stabilised organic pigment.

USE/ADVANTAGE - An optical information recording medium

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(Translation)

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Filing date: July 19, 1989  
JP Patent Laid-open No. Hei 3-51182  
Laid-open date: March 5, 1991  
Applicant: Matsushita Denki Sangyo Kabushiki Kaisha

## SPECIFICATION

## 1. Title of the invention

Optical recording medium

## 2. Claims

(1) An optical recording medium comprising a transparent substrate and, provided thereon, a record layer containing a ~~light stabilized organic coloring matter comprising a bonded product of anion of an electron acceptable~~ metal complex salt compound of azo series and cyanine dye cation having absorption at the area of the wave length of the light for recording.

(2) An optical recording medium according to claim (1), having a structure in which at least a record layer, a reflecting layer comprising a metal, and a protection layer are laminated in that order on the transparent substrate.

(3) An optical recording medium according to claim (1), having a structure in which at least a record layer, an intermediate layer comprising a transparent resin, a reflecting layer comprising a metal, and a protection layer are laminated in that order on the transparent substrate.

(4) An optical recording medium according to claim (1), having a structure in which at least a record layer, an intermediate layer comprising a resin, and a protection layer are laminated in that order on the transparent substrate.

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further, those of reloading type. What is common to these disc-form optical recording media is that a record layer comprising an organic or inorganic material is provided onto a transparent substrate, such as a polycarbonate, and physical or chemical change of substance is caused by irradiation of light, and thus caused change is optically read and reproduced.

Explanations will be given, taking, as a prior art example, a heat-mode postscript type optical recording medium wherein an organic coloring matter is used. In this heat-mode optical recording medium, the light for recording is utilized as heat, with which a part of the medium is melt removed to form a small hole called as pit, and information is recorded by means of thus formed pits (See, for instance, "Hikari Kiroku Gijutsu and Zairyo" (Optical Recording Technology And Materials)", pages 32-42).

First, a transparent substrate comprising an acrylic or polycarbonate resin or the like is made. On this transparent substrate, there is formed a record layer comprising a coloring matter having a large absorption in the area of the wave length of semiconductor laser, for instance a cyanine dye. When this record layer is irradiated in minute spots with a laser light as recording light source, the irradiated portions make minute holes, thereby information is recorded. In order to enhance reflectance when occasion demands, a reflecting layer, and further a protection layer, may sometimes be provided.

- Problems to be solved by the invention -

Optical discs having an organic coloring matter as record-

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(5) An optical recording medium according to claim (1), having a structure in which at least a record layer and a protection layer are laminated in that order on the transparent substrate.

(6) An optical recording medium according to any one of claims (1)-(5), wherein the record layer contains a light stabilized organic coloring matter comprising a bonded product of anion of an electron accept<sup>or</sup>~~able~~ metal complex salt compound of azo series and cyanine dye cation having absorption in the area of the wave length of the light for recording, and at least one coloring matter having an absorption maximum different from that of the light stabilized coloring matter.

(7) An optical recording medium according to any one of claims (1)-(6), wherein the recording layer contains a resin.

### 3. Detailed description of the invention

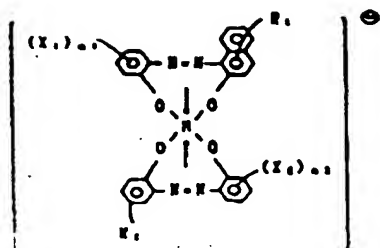
#### - Industrial fireld of utilization -

The present invention relates to an optical recording medium which write and read signals by reflection or transmission of light beam.

#### - Prior art -

Optical discs are among optical recording media which are presently broadly commercialized, and their representatives may be compact discs and optical video discs. It can be said that at present these discs are extensively studied, including those of reproduction-only type in which music or image information has been previously recorded, those of so-called postscript type into which information can be written into a disc seriatim and,

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wherein  $X_1$  and  $X_2$  are nitro or halogen,  $n_1$  and  $n_2$  are integers of from 1 to 3,  $R_1$  and  $R_2$  are amino, monoalkylamino, dialkylamino, acetylamino, benzoylamino including substituted benzoylamino, it being possible for  $X_1$  and  $X_2$ ,  $n_1$  and  $n_2$ , and  $R_1$  and  $R_2$  to be the same or different, and M is chromium or cobalt.

- Function -

The present invention can provide optical recording media which are stable against environmental lights and the repeatedly irradiated reproduction light by providing, according to the above-mentioned constitution, a record layer containing a light stabilized organic coloring matter comprising a bonded product of anion of an electron acceptable metal complex salt compound of azo series of the formula (1) and cyanine dye cation having absorption at the area of the wave length of the light for recording.

- Examples -

Figure 1 is a section view of an optical recording medium in which a record layer according to the present invention is provided onto a transparent substrate and on which information is recorded, in said figure 1 being the transparent substrate, 2 being a base coat layer, 3 being the record layer and 4 being a recording pit. Figure 2 shows the absorption spectrum of the

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ing film had problems that the reflectance of the thin recording film is lower than that of a metallic recording film, that plastic substrates elute due to the solvent used in the preparation of the film, that they do not have definite threshold values and thermally or optically deteriorate by the light for reproduction and by environmental lights, that they have inferior humidity resistance because of crystallization of the organic coloring matter when such a coloring matter has been applied as film, and that, because of their low heat resistance, they are discolored by heat or signals are impaired due to deformation of pits during recording.

In view of the above-mentioned problems, the present invention is to provide an optical recording medium which is stable against the reproduction light which is repeatedly irradiated and against environmental lights and which have good humidity resistance.

~~Means to solve the problems~~ -

In order to solve the above-mentioned problems, the optical recording media of the present invention comprises a transparent substrate, and provided thereon, a record layer containing a ~~light stabilized organic coloring matter comprising a bonded product of anion of an electron acceptable metal complex salt compound of azo series of the formula shown below and~~ cyanine dye cation having absorption at the area of the wave length of the light for recording.

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referred to as open type optical recording medium, and one comprising a transparent substrate 1 and a record layer 3, an aluminum reflecting layer 6 and a protection layer 7 formed thereon in that order is referred to as adhesion type optical recording medium. First, explanations will be made on the method for the production of the open type optical recording medium containing the record layer 3 according to present invention. An intermediate of cyanine dye cation which is neutral (a hydroxide) is dissolved in a methyl ethyl keton solution and, to the resultant solution, there added an electron acceptable metal complex salt compound of azo series of the formula 1, which concretely is a chromium metal complex salt compound of the formula 2 shown below produced by Hodogaya Kagaku Kogyo K.K., in an equimolar amount and dissolved. The resultant solution is allowed to react with stirring, condensed and recrystallized to obtain the light stabilized organic coloring matter according to the present invention. On a base coat layer 2 formed on a transparent polycarbonate substrate 1, a solution of thus obtained light stabilized organic coloring matter is applied and dried to obtain the open type optical recording medium (A) of the present invention. An open type optical recording medium (B) as comparative example is produced by applying, onto a transparent polycarbonate substrate 1 with a base coat layer, a solution obtained by dissolving a conventional cyanine dye in a dichloroethane solution, and drying thus applied coat. Finally, the adhesion type optical recording medium (C) of the present invention was produced by analo-

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optical recording medium in which the record layer according to the present invention is provided onto a transparent substrate. Figure 3 shows the recording properties, Figure 4 shows light resistance test results and Figure 5 shows the repetitive reproduction properties, in said figures 5 being an intermediate layer, 6 being a reflecting layer, 7 being a protection layer, and the other numbers having the same meanings as shown in Figure 1. Figure 10 shows humidity resistance test results of the optical recording media of the present invention.

The following examples will concretely illustrate the optical recording media of the present invention.

(Concrete Example 1)

In Figure 1, a polysiloxane base coating solution was applied by spin coating method onto a transparent polycarbonate substrate of 1.2 mm in thickness and 120 mm in diameter, and dried to form a base coat layer 2. On thus formed layer 2, a record layer according to the present invention was further formed to produce an optical recording medium. As a comparative example, an optical recording medium was also produced by further forming on said layer 2 a record layer 3 containing a conventional cyanine dye alone. Further, an optical recording medium was also produced by forming a record layer 3 according to the present invention, an aluminum reflecting layer 6 and a clear protection layer 7 in that order on the above-mentioned substrate having the base coat layer, as shown in Figure 6. Hereinafter, an optical recording medium comprising a transparent substrate 1 and only a record layer 3 formed thereon is



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(3) Repetative reproduction properties:

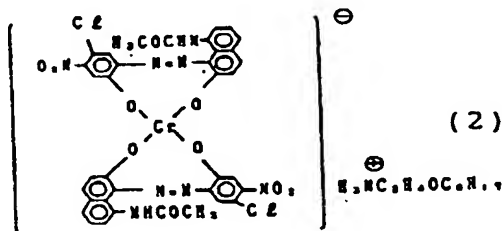
Repetative reproduction properties of the optical recording media (A) and (C) of the present invention, as well as those of the conventional open type optical recording medium (B), are shown in Figure 5. For evaluation, an OMS-100 deck produced by Nakakmichi was used. In the conventional medium (B), obvious deterioration is seen at reproduction power of 0.4 mw or greater. In the open type medium (A), however, the power at which deterioration begins became higher than the conventional medium to 0.5 mw. In the adhesion type medium (C), further, a remarkable property improvement was seen. The following explanation may be made on such a property improvement derived from the adhesion type. In the open type optical recording media, the larger the absorption at wave length of the light for reproduction becomes, the greater the heat accumulation in the record layer becomes and the worse the properties become. It can be said that, with the employment of the adhesion type structure, like the optical recording medium (C) of the present invention, the accumulation of heat in the record layer decreased because of the heat releasing effect of the aluminum reflection layer, and thereby the properties were improved remarkably.

(4) Humidity resistance:

When conventional cyanine dyes are kept in humid conditions, their humidity resistant properties becomes worse due to crystallization or the like. However, the optical recording media in which the record layer according to the present invention is provided have good humidity resistant properties, as shown in Figure 10.

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gously forming a record layer 3 comprising the light stabilized organic coloring matter according to the present invention on a transparent polycarbonate substrate 1 with a base coat layer, depositing aluminum thereon and then forming a protection layer 7 by spin coating method.



(1) Recording properties:

Recording properties determined in regard to the optical recording media (A), (B) and (C) are shown in Figure 3. Evaluation was made using an OMS-1000 deck produced by Nakamichi. Recording condition is 1.3m/s. 200 kHz, and reproduction power is 0.4 mw. It is seen that the optical recording media of the present invention, both open type and adhesion type, show a high C/N value equal to that of the open type optical recording medium having the conventional cyanine dye.

(2) Light resistance:

Using a xenon long life fadeometer, light resistance tests were conducted on the optical recording medium (A) of the present invention and the conventional optical recording medium (B). The results are shown in Figure 4. As evident from Figure 4, the conventional medium discolors after 20 hours, but a great improvement of light resistance is seen in the medium of the present invention.

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no limitation in the disc shape.

- Effect of the invention -

As described above, the present invention can provide optical recording media which are stable against environmental lights and against the reproduction light which is repeatedly irradiated and which have good humidity resistance, by adopting the record layer containing a light stabilized organic coloring matter comprising a bonded product of anion of an electron acceptable metal complex salt compound of azo series and cyanine dye cation having absorption at the area of the wave length of the light for recording.

4. Brief explanation of the drawings

Figure 1 is a section view of an optical recording medium in which the record layer according to the present invention is provided onto a transparent substrate and on which information is recorded. Figure 2 is a diagram showing the absorption spectrum of the optical recording medium in which the record layer according to the present invention is provided onto a transparent substrate. Figure 3 is a diagram showing the recording properties, Figure 4 is a diagram showing light resistance test results and Figure 5 is a diagram showing the repetative reproduction properties. Figures 6-9 are section views showing the structures of the optical recording media of the present invention. Figure 10 is a diagram showing humidity resistance test results of the optical recording media of the present invention.

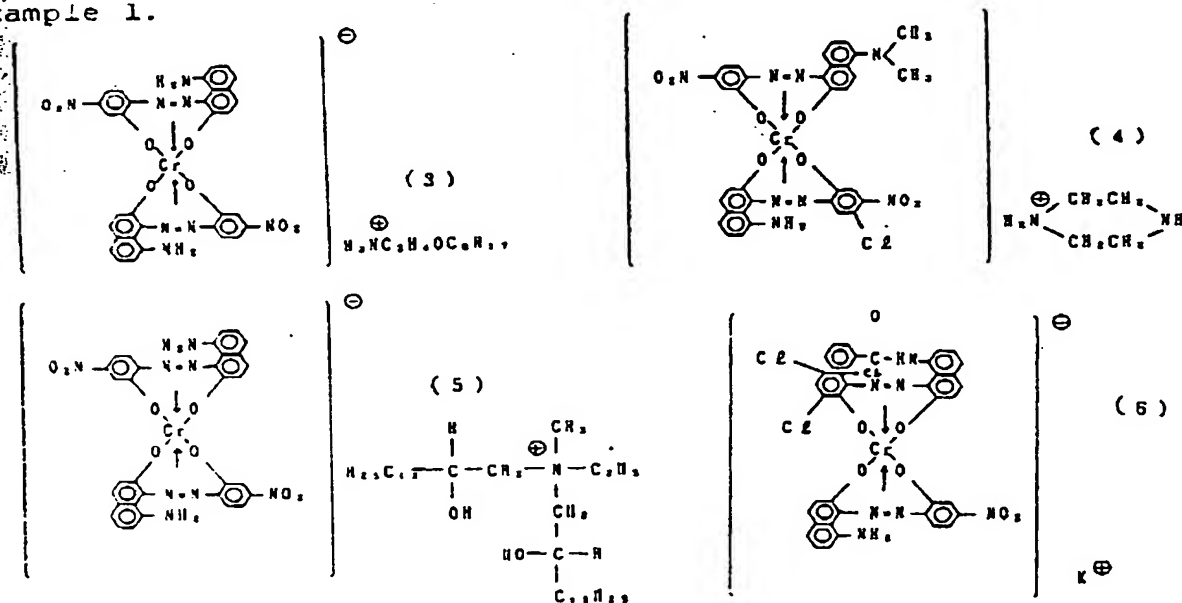
1 ... Transparent substrate

2 ... Base coat layer

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## (Concrete Examples 2-5)

From chromium metal complex compounds of the formulae 3-6 shown below produced by Hodogaya Kogyo K.K., light stabilized organic coloring matters were obtained in the manner analogous to that in Concrete Example 1. Four open type optical recording media of the present invention, in which thus obtained coloring matters are used, were subjected to evaluation of recording properties, light resistance, repetitive reproduction properties and humidity resistance, and the evaluation results were almost the same as those of the open type optical recording medium (A) of the present invention obtained in Concrete Example 1.



The optical recording media of the present invention may have a structure having an intermediate layer, a reflection layer and a protection layer, as shown in Figures 7-9. They may of course have an air-sandwich structure. The presence or absence of the base coat layer is not critical, and there is

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Fig. 7

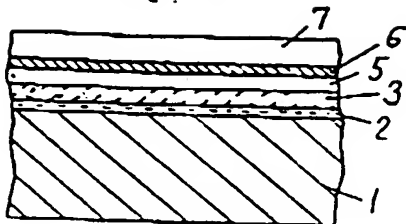


Fig. 9

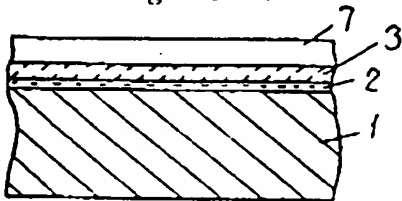


Fig. 8

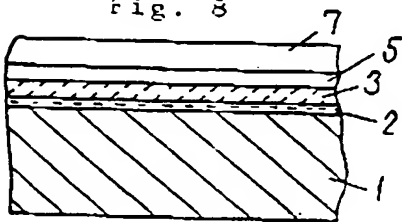
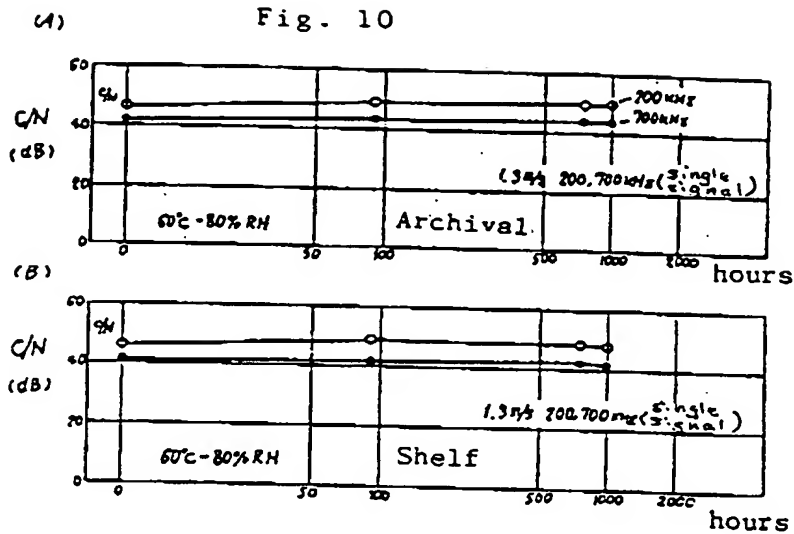


Fig. 10



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- 3 ... Record layer
- 4 ... Recording pit
- 5 ... Intermediate layer
- 6 ... Reflecting layer
- 7 ... Protection layer

Fig. 1

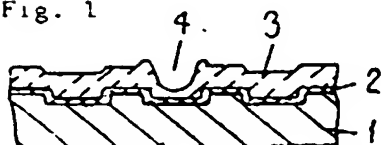


Fig. 2

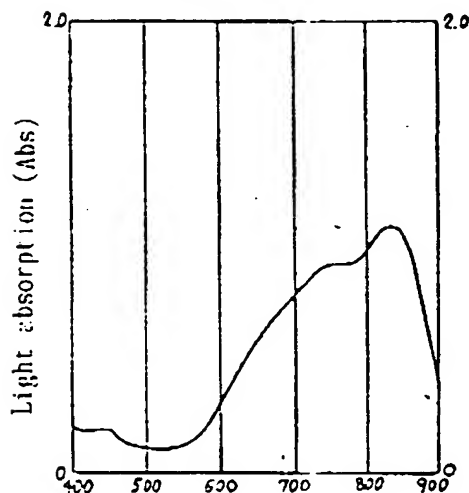


Fig. 3

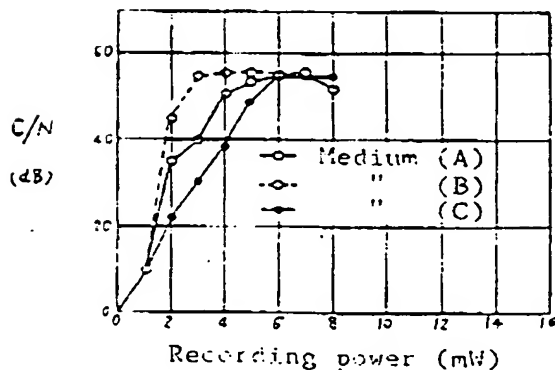


Fig. 4

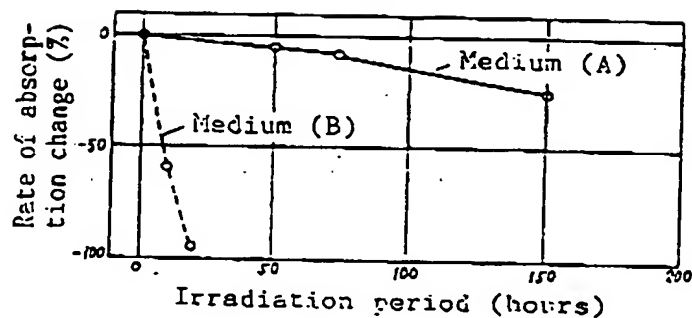


Fig. 5

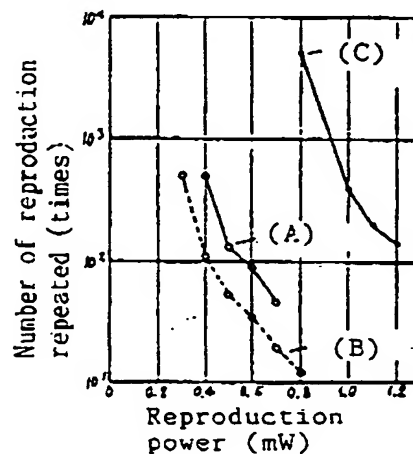


Fig. 6

